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Cooper Engineered Products
Bowling Green, Ohio

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PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

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ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Dino Mattorano and Doug Trout, of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Field assistance was provided by Alan Echt, Kevin Hanley, and Boris Lushniak of DSHEFS. Analytical support was provided by Data Chem Laboratories, Salt Lake City, Utah; and Measurements Research Support Branch, Division of Physical Science and Engineering. Desktop publishing was performed by Nichole Herbert. Review and preparation for printing was performed by Penny Arthur.

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August 1998

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SUMMARY

On September 13, 1996, the National Institute for Occupational Safety and Health (NIOSH) received a management request for a health hazard evaluation (HHE) at Cooper Engineered Products, in Bowling Green, Ohio. The request noted concerns about workers' exposure to a new, two-component, water-based polyurethane paint (water-based polyurethane paint with polytetrafluoroethylene and a polyfunctional aziridine cross-linker) that is applied to automotive/truck rubber seals (vehicle sealing) on the dual durometer (DD) extrusion lines. Health effects described in the request included skin and upper respiratory problems. On October 16, 1996, NIOSH industrial hygienists conducted an initial site visit. Area air samples were collected on thermal desorption (TD) tube media to qualitatively identify volatile organic compounds (VOC). Bulk samples of the water-based polyurethane paint were also collected. A follow-up site visit was conducted on March 25-26, 1997, to collect additional air samples. On January 21, 1997, NIOSH medical officers conducted a site visit and questionnaire survey. In April and May 1997, skin patch testing was performed to identify employees with allergic contact dermatitis.

N-methyl pyrrolidone (NMP) was used as a surrogate for exposure to the water-based polyurethane paint because it was a major component of the bulk paint samples and the TD tube air samples. Utility incentives (those who work at end of DD lines) who worked with the paint or in the paint booths (adjusting spray guns or changing filters) had mean inhalation exposures to NMP (0.15 parts per million [ppm]) almost 4 times greater than workers who did not work with paint (0.04 ppm). Inhalation exposures of operators to NMP were similar to those of utility incentives who did not work with the paint or paint booths. Workers in the DD department may also be exposed to low levels of propylene glycol, carbon disulfide, and xylenes.

Area air samples were collected for isocyanates at various locations on the DD lines because the paint was made with a polyisocyanate. All air sample concentrations were below the minimum detectable concentration (MDC) of 1.6 $\mu\text{g}/\text{m}^3$. Area and personal breathing zone (PBZ) air samples were collected for n-nitrosamines on both cascade lines (salt baths) and two DD lines. All air sample concentrations were below 0.028 $\mu\text{g}/\text{m}^3$ (MDC).

Utility incentives were dermally exposed to irritants and a sensitizer in the paint, especially when working in the paint booths, changing filters, or adjusting the spray guns. Only one worker was observed wearing gloves.

Two DD workers, both of whom had a history of work-related skin rashes, had skin reactions suggestive of allergy to accelerators present in the rubber used at Cooper.

NIOSH investigators identified two DD workers allergic to accelerators present in the rubber. These workers may also have an irritant component to their skin problems. Workers were dermally exposed to irritants and a sensitizer in the water-based polyurethane paint when changing filters and adjusting the spray guns in the paint booths. Mean inhalation exposures to NMP were below 1 part per million, and all isocyanate concentrations were less than $1.6 \mu\text{g}/\text{m}^3$ (the MDC). Recommendations are made to minimize dermal exposures to rubber products, to decrease exposure to the irritants and sensitizer in the paint, and to provide a system for the evaluation, reporting, and surveillance of dermatologic conditions.

Keywords: SIC 3061 (Molded, Extruded, and Lathe-Cut Mechanical Rubber Goods) vehicle sealing, automotive/truck rubber seals, water-based polyurethane paint, polyfunctional aziridine, N-methyl pyrrolidone, NMP, N-nitrosamines, isocyanates, skin patch testing, allergic contact dermatitis

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INTRODUCTION

On September 13, 1996, the National Institute for Occupational Safety and Health (NIOSH) received a management request for a health hazard evaluation (HHE) at Cooper Engineered Products, in Bowling Green, Ohio. The request noted concerns about workers' exposure to a new, two-component, water-based polyurethane paint (water-based polyurethane paint with polytetrafluoroethylene and a polyfunctional aziridine cross linker) that is applied to automotive/truck rubber seals (vehicle sealing) on the dual durometer (DD) lines (extrusion area). Health effects described in the request included skin and upper respiratory problems.

On October 16, 1996, NIOSH industrial hygienists conducted an initial site visit. Area air samples were collected on thermal desorption tube media to qualitatively identify volatile organic compounds (VOC) in the DD department. Bulk samples of the water-based polyurethane paint were also collected. Based on the information obtained from the initial site visit, NIOSH industrial hygienists conducted a followup site visit on March 25–26, 1997, to collect additional air samples.

On January 21, 1997, NIOSH medical officers conducted a visit and questionnaire survey. Findings were summarized in a letter to management and employee representatives dated February 10, 1997. In April and May 1997, NIOSH medical officers conducted follow-up site visits to conduct skin patch testing to identify allergic contact dermatitis. Findings were summarized in a letter to management and employee representatives dated June 10, 1997.

BACKGROUND

The DD department, the largest area of the plant, produced weather stripping that goes around automobile doors. Approximately 155 workers were employed over three shifts. The vehicle sealing was produced through eight DD extrusion lines, three

flocking extrusion lines, and two cascade extrusion lines.

On the DD lines, the continuous process began with wire mesh being formed into a channel while dense rubber was extruded around it and sponge rubber was extruded on top of it. Following extrusion, the vehicle sealing was cured by mechanically pulling it through gas or electric ovens. After the first series of ovens, a limited amount of a water-based polyurethane paint was sprayed onto the vehicle sealing in an enclosed paint booth that was exhausted outside. The vehicle sealing was further cured through another series of gas or electric ovens. As the vehicle sealing exited the ovens, it was cleaned with water and high pressure air. In some cases, small holes were drilled into the sponge rubber. At the end of the line, the vehicle sealing was automatically cut into specified lengths.

Each DD line had one operator and two utility incentives. In general, operators controlled the line and worked from the beginning of the line to the ovens. Work activities included feeding dense and sponge rubber and wire mesh into the extruder. In some cases, operators would clean the spray guns and change the filters in the paint booths. Utility incentives worked from the ovens to the end of the lines. Work activities included removing vehicle sealing from the line (clipping the ends with pliers, and boxing the vehicle sealing), mixing the paint, adjusting/cleaning the spray guns, and changing the filters in the paint booths. The focus of this investigation was the utility incentives because they tended the paint booths (mix paint, adjust and clean paint nozzles, change air filters), handled the vehicle sealing following paint application and curing, and had reported the majority of the skin problems.

The paint consists of a water-based polyurethane component and a polyfunctional aziridine cross-linker (cx 100).¹ Aziridine has been reported to be a skin irritant and sensitizer.^{2,3,4} The compound cx100 is composed of aziridine uncontaminated by other known sensitizers.⁵ An allergic response to aziridine, demonstrated in skin patch testing with aziridine cx100, has been reported in two printing

industry workers.⁵ The water-based polyurethane component of the paint is made up in part of N-methyl pyrrolidone (1-methyl-2-pyrrolidone) (NMP) and propylene glycol (1,2 propanediol), which are irritants.^{6,7,8} The proprietary polyurethane resin is made by reacting stoichiometric amounts of polyisocyanate and polyol. The manufacturer reports that no free isocyanate is present after the reaction; but, if there were, the isocyanate would be immediately consumed by reaction with water when the resin is converted to a water-based resin.⁹

METHODS

Industrial Hygiene

During the initial industrial hygiene site visit, thermal desorption (TD) tubes were used to qualitatively identify airborne volatile organic compounds (VOCs). Area air samples were collected near the exterior of the paint booths on DD lines 2 and 5 for approximately 90 minutes. These samples were collected at a flow rate of 50 cubic centimeters of air per minute (cc/min) using low-flow pumps. Results of the thermal desorption tube analysis revealed NMP, propylene glycol, carbon disulfide, xylene, triethylamine, 2-ethyl hexanoic acid, propane, and C₁₁-C₁₂ aliphatic hydrocarbons as major components. Trace levels of N-nitrosomorpholine and N-nitrosobutylamine also were indicated. Analysis of the bulk paint sample (mixture of both components) revealed NMP and propylene glycol as major components.

During the second industrial hygiene site visit, charcoal tubes were used to collect personal breathing zone (PBZ) air samples for NMP analysis. This analyte was chosen as an indicator of relative levels of paint exposure based on results of the TD tubes and the bulk sample analysis described above. These samples were collected at a flow rate of 50 cc/min using low-flow pumps. Each sample was analyzed by a gas chromatograph/flame ionization detector using an HP6890 gas chromatograph containing a 30 meter (m) Rtx-5 amine (0.32 millimeter [mm] inside diameter,

1.00 micrometer [μm] film) fused-silica capillary column. The analytical limit of detection (LOD) for NMP was 0.26 microgram (μg)/sample, which equates to a minimum detectable concentration (MDC) of 0.006 parts per million (ppm) using a maximum sample volume of 11.4 liters. The analytical limit of quantitation (LOQ) for NMP was 0.61 μg/sample which equates to a minimum quantifiable concentration (MQC) of 0.01 ppm using a maximum sample volume of 11.4 liters. PBZ air samples were collected over two periods, 7:00 a.m. to 10:30 a.m. and 10:30 a.m. to 2:00 p.m. on both March 25 and 26, 1997.

Area and PBZ samples were collected for N-nitrosamines in the DD department because trace levels were found on the TD tubes. Air samples were collected on Thermosorb-N[®] tubes at a flow rate of 2 liters per minute (Lpm). The samples were analyzed for seven analytes: N-nitrosodimethylamine, N-nitrosodiethylamine, N-nitrosodipropylamine, N-nitrosodibutylamine, N-nitrosopyrroline, N-nitrosopiperidine, and N-nitrosomorpholine. A micromass autospec high resolution mass spectrometer operating in the high-resolution selected-ion-monitoring mode and a Carlo-Erba model 8065 gas chromatograph equipped with a 30 m by 0.25 mm HP-INNOWAX capillary column were used for all measurements. The analytical LOD was 0.024 μg/tube, which equates to a MDC of 0.02 micrograms per cubic meter (μg/m³) using a maximum sample volume of 1034 liters. Samples were collected between 6:30 a.m. and 3:30 p.m. for approximately eight hours.

Area air samples were collected for isocyanates throughout the DD department. The midjet impingers were calibrated at a flow rate of one Lpm. The samples were analyzed for isocyanates using NIOSH analytical method 5522.¹⁰ The analytical LOD was 0.07 μg/sample, which equates to an MDC of 1.6 μg/m³ using a maximum sample volume of 428 liters. The analytical LOQ was 2.1 μg/sample, which equates to an MQC of 4.9 μg/m³ using a maximum sample volume of 428 liters. Samples were collected between 8:00 a.m. and 3:30 p.m.

Medical

A questionnaire survey was performed at the Cooper plant during the site visit in January 1997. Conversations with management and employee representatives prior to the site visit had revealed that the medical conditions of primary concern among employees of the DD lines were related to the skin. A questionnaire that included questions regarding skin symptoms and work and medical history was made available to 154 of 155 workers in the DD department; 57 (37%) completed and returned the questionnaires. Of the 57 respondents, 24 (42% of respondents, 15% of all workers) reported work-related skin problems in the six months prior to the site visit. A work-related skin problem was defined as any dermatitis or skin rash that the worker identified as potentially related to his or her work. At the time of the site visit, three workers had active skin eruptions consistent with contact dermatitis. Prior to the NIOSH site visit, Cooper management had identified 10 DD workers who had reported skin problems potentially related to the workplace; 4 of those 10 did not participate in the NIOSH questionnaire survey.

On April 18 and 23, 1997, the NIOSH medical officer met with management and union representatives, and with the 28 workers identified above, to explain the purpose, technique, and interpretation of skin patch testing to diagnose allergic contact dermatitis. Thirteen of the 28 workers agreed to participate in skin patch testing. In addition, two other workers with dermatitis thought to be work-related were identified employee representatives and management at the time the skin patch testing was being conducted, and they agreed to participate as well. Therefore, a total of 15 workers provided informed consent and participated in the skin patch testing.

The skin patch testing (which was approved by the NIOSH Human Subjects Review Board) was performed using a standard, commercially available, skin patch panel of 20 substances, and a panel of 4 substances prepared by NIOSH personnel. The standard panel is made up of common allergens

(including several common rubber additives); a list of all substances used in the testing is presented in Appendix 1. The four substances made up in the NIOSH laboratory were aziridine cross-linking agent (0.1% in both water and petroleum jelly), the water-based polyurethane component of the paint (0.1% in water), and a 1:36 mixture of the cross-linking agent and the polyurethane component (which is the same ratio as that used at Cooper) (0.1% in water). The concentrations (0.1%) were the same as those used in previous patch testing with the aziridine cross-linking agent.^{5,11} The NIOSH team performing the testing included a NIOSH medical officer who is a board-certified dermatologist.

The potential allergens were applied to the participants' upper backs using Finn® chambers on Scanpor® tape, with an outer layer of tape (also hypo-allergenic) used to cover the Scanpor® tape. Within several hours after the first four skin patch tests were applied, it was evident that the outer tape had become loosened from the back of two participants – most likely due to sweating. The first four participants were called back and the outer layer of tape was re-applied after first applying to the skin a thin coat of tincture of benzoin, an adhesive used in many medical applications. Three subsequent participants (for a total of seven) had the outer tape covering the Scanpor® applied in this manner. Approximately 30 minutes after the benzoin and outer tape were applied, two participants returned to the testing area reporting discomfort and itching/burning at the site of the tape. Examination of those areas revealed erythema (redness). The two participants were experiencing an irritant-type reaction on the skin where the benzoin and outer tape had been applied. For those two participants, the outer tape was removed, the benzoin washed off with water, and the outer tape re-applied to cover the Scanpor® tape (which had remained in place throughout). All persons who had benzoin applied were rechecked within 30 – 60 minutes of application, and no others demonstrated any reaction to the benzoin or the tape. Benzoin was not used in subsequent participants who had not yet had their skin patches applied.

The patches were applied on Monday, May 5. Participants were instructed to keep the patches dry, to re-tape the patches as needed, and to notify the NIOSH medical officer of any problems, or if any medications, such as anti-histamines or topical steroids, were used. All participants continued their usual work activities. The patches were removed on Wednesday, May 7, and the first interpretation was done. The second (final) interpretation of the patch tests was done on Friday, May 9. The patch test sites were interpreted using a standard scale of 1+ to 3+, with 1+ (minor skin redness) representing an irritant response, and 2+ (redness, mild swelling, and mild to moderate vesicle formation) and 3+ (redness, swelling, and larger vesicle or bullae formation) representing allergic reactions. All participants were told their test results on May 9 and were given a written copy of these results. The significance of the testing for each individual was discussed privately; participants with positive tests were given information sheets concerning the allergens to which they reacted.

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not

considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent becomes available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH recommended exposure limits (RELs)¹², (2) the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®)¹³, and (3) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs).¹⁴ NIOSH encourages employers to follow the OSHA PELs, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criterion. The OSHA PELs reflect the feasibility of controlling exposures in various industries where the agents are used, whereas NIOSH RELs are based primarily on concerns relating to the prevention of occupational disease. It should be noted when reviewing this report that employers are legally required to meet those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits (STEL) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

Industrial Hygiene

N-methyl pyrrolidone, classified as a cyclic amide with a mild amine odor, is miscible in water, combustible, and has a relatively low vapor pressure of 0.334 millimeters of mercury (mm Hg) at 25 °C.^{7,15} Exposure to NMP may produce mild skin irritation and severe eye irritation on contact. Inhalation studies with laboratory animals showed that rats exposed to a concentration of 246 ppm for 6 hours a day for four weeks experienced lethargy,

difficulty breathing, and increased mortality.¹⁶ No carcinogenic effects were observed in a 2-year study of experimentally exposed rats.¹⁶ There are little data available on the effects of exposure on humans, and occupational exposure data are also lacking. However, one investigation, in the semiconductor industry, reported that workers exposed to NMP experienced severe eye irritation and headaches at concentrations as low as 0.7 ppm for periods as short as 30 minutes.¹⁷ Based on these findings, the investigators recommended controlling worker exposure to NMP to less than 0.1 ppm.

Official occupational exposure standards have not been established for NMP; there is currently no OSHA PEL or NIOSH REL. Previously, the ACGIH had proposed a TLV of 100 ppm for NMP.¹⁸ The proposal, however, was dropped, apparently because the vapor pressure of NMP was so low, it was felt the proposed TLV could not be exceeded.¹⁹

Medical

Occupational skin diseases can manifest themselves in a variety of ways. The most common forms include contact dermatitis, which includes irritant contact dermatitis and allergic contact dermatitis. Many references on occupationally-related skin disorders are available.^{20,21,22} Epidemiologic data show that contact dermatitis makes up 90–95% of all occupational skin diseases.^{23,24,25} Contact dermatitis (both irritant and allergic) is an inflammatory skin condition caused by skin contact with an exogenous agent or agents, with or without a concurrent exposure to a contributory physical agent (e.g., ultraviolet light). It is widely accepted that of all contact dermatitis, 80% is due to a nonimmunologic reaction to chemical irritants (irritant contact dermatitis) and 20% to allergic reactions (allergic contact dermatitis). Irritant contact dermatitis is a cutaneous inflammation resulting from a direct cytotoxic effect of a chemical or physical agent, while allergic contact dermatitis is a type IV (delayed or cell-mediated) immune reaction. Any chemical, in sufficient concentration and under the right conditions, can cause irritation. Only certain chemicals are allergens, and only a proportion,

usually small, of people are susceptible to them. Complete reviews of irritant contact dermatitis and allergic contact dermatitis, and lists of irritants and allergens, are available in other sources.^{20,22,26,27}

In dermatitis, the skin initially turns red and can develop small, oozing blisters (vesicles) and bumps (papules). After several days, crusts and scales form. Stinging, burning, and itching may accompany the rash. With no further contact, the rash usually disappears in one to three weeks. With chronic exposure, deep cracking (fissures), scaling, and discoloration of the skin (hyper pigmentation) can occur. Exposed areas of the skin, such as hands and forearms, which in most occupational settings have the greatest contact with irritants or allergens, are most commonly affected. If the chemical gets on clothing, it can produce rashes at areas of greatest contact, such as thighs, upper back, armpits, and feet. Irritants and allergens can be transferred to remote areas of the body (such as the trunk or genitalia) by unwashed hands or from areas of accumulation (such as under rings or in between fingers). It is often impossible to clinically distinguish irritant contact dermatitis from allergic contact dermatitis, as both can have a similar appearance and both can be clinically evident as an acute, subacute, or chronic condition.

The work-relatedness of skin diseases may be difficult to prove. Guidelines are available for assessing the work-relatedness of dermatitis,²⁸ but even with these guidelines the diagnosis may be difficult. The diagnosis is based on the medical and occupational histories and physical findings. In many instances, allergic contact dermatitis can be confirmed by skin patch tests using specific standardized allergens or with nonirritating dilutions of chemicals specific to an individual workplace.²⁶ An example of the guidelines to determine work-relatedness of dermatitis follow:²⁸

1. Is the clinical appearance consistent with contact dermatitis?
2. Are there workplace exposures to potential cutaneous irritants or allergens?

3. Is the anatomic distribution of dermatitis consistent with cutaneous exposure in relation to the job task?
4. Is the temporal relationship between exposure and onset consistent with contact dermatitis?
5. Are nonoccupational exposures excluded as probable causes?
6. Does dermatitis improve away from the exposure to the suspected irritant or allergen?
7. Do patch tests or provocation tests identify a probable causal agent?

Because people with contact dermatitis can develop long-term dermatologic problems, prevention is key. Strategies in the prevention of contact dermatitis include identifying allergens and irritants; substituting chemicals that are less irritating/allergenic; establishing engineering controls to reduce exposure; utilizing personal protective equipment (PPE), such as gloves and special clothing, appropriately; emphasizing personal and occupational hygiene; and establishing educational programs to increase awareness in the workplace.^{25,29} The introduction of PPE must be considered carefully since it may actually create problems by occluding allergens or irritants against the skin or by directly irritating the skin. Similarly, excessive use of soaps and detergents can result in irritant contact dermatitis.³⁰ The effectiveness of gloves depends on the specific exposures and the types of gloves used. The effectiveness of barrier creams is controversial,³¹ and at times workers using barrier creams may have higher prevalence rates of contact dermatitis compared to those who do not use the creams.³²

RESULTS/DISCUSSION

Industrial Hygiene

Air sampling

Results of the PBZ air samples for NMP are presented in Table 1. Workers on DD lines 3 and 8 were not monitored because the water-based polyurethane paint was not used on these lines during the survey. Workers with the highest exposures were the utility incentives who entered the paint booths to adjust the spray guns and/or to change the air filters. The mean NMP exposure for these individuals was 0.15 ppm with a range from 0.01 to 1.27 ppm. For the utility incentives who did not work with the paint or paint booths, exposures ranged from 0.01 to 0.15 ppm with a mean exposure of 0.04 ppm. The two highest exposures (0.15 and 0.12 ppm) were collected from utility incentives who worked near the paint mix areas – at the end of DD lines 1 and 2 near the paint mix area.

Area air samples were collected for NMP inside and outside the paint booths, near the cascade line paint mix area, and near the lunch room. Sampling results are presented in Table 1. The mean NMP concentration outside the paint booth (0.05 ppm) was lower than the concentration inside (12 ppm). Based on this information and visual observations of the paint booths, the exhaust systems appeared to be in good working condition. The NMP detected outside the booths was likely due to paint buildup on the filters (decreased air flow in booth) and the continuous opening and closing of the booth doors to adjust the spray guns. The mean NMP concentration of the area air samples collected at the paint mix area near cascade line 2 was 0.10 ppm. Area air samples collected near the lunch area resulted in air concentrations which ranged from < 0.006 ppm (MDC) to 0.03 ppm.

Task-based PBZ air samples were also collected during this investigation. The first job task observed was a utility incentive changing air filters in a paint

booth. The worker wore cotton gloves and a half-face, air-purifying respirator with dual organic vapor and dust/mist cartridges. Before entering the paint booth, the worker removed and replaced the filter with new one. (The worker had facial hair, however, that interfered with the respirator facepiece and face seal.) The duration of the task was approximately 5 minutes. The PBZ air sample concentration for NMP was 0.19 ppm. NIOSH investigators observed paint on the worker's hands and arms. Dermal exposure was from removing the filters which were saturated with paint and from touching/bumping surfaces inside the paint booth, all of which were covered with paint residue.

The second job task observed was a utility incentive mixing the paint and filling the paint booth canister. The worker wore nitrile gloves while performing these tasks, but no other PPE. First, limited amounts (ounces) of the polyfunctional aziridine cross-linker were poured into a large bucket (gallons) of the water-based polyurethane component of the paint (the mixing location was near DD lines 1 and 2). A pneumatic mixer was used to blend the paint. Once mixed, the paint was poured into another container through a fine screen to remove any large particles. The mixture was then placed on a small push cart and rolled to a paint booth and poured into the paint canister. During this twelve-minute task, the worker's PBZ air sample concentration was below 0.006 ppm (MDC). The worker did not have any evidence of dermal exposure to the paint. However, paint residue was observed on all mixing equipment, as well as on the concrete floor, indicating potential dermal exposure from splashes or spills.

Area samples were collected for isocyanates at various locations on the DD lines that used the water-based polyurethane paint. Sample locations included inside and outside the paint booths, at the end of the lines where utility incentives worked, and in the paint mix area near cascade line 2. Isocyanate concentrations were all below $1.6 \mu\text{g}/\text{m}^3$ (MDC).

Area and PBZ air samples were collected for N-nitrosamines on both cascade lines (salt baths) and two DD lines. Area sample locations on the DD

lines included after the extruder, after the first set of curing ovens, and after the rubber seal drilling and cutting mechanisms. On the cascade lines, area air samples were collected after the extruder, after the first set of salt baths, and after the vehicle sealing cutting mechanism. PBZ air samples were collected from one operator and two utility incentives that worked on the cascade lines. All N-nitrosamine concentrations were below $0.028 \mu\text{g}/\text{m}^3$ (MDC).

Observations

Several noteworthy observations were made during the NIOSH investigation. Utility incentives were in continuous dermal contact with the cured vehicle sealing throughout the work shift. They removed vehicle sealing from the end of the DD line, and clipped the ends with pliers, and then boxed the vehicle sealing. Only one worker was observed wearing gloves (nitrile) while working with the vehicle sealing.

As described previously, workers were dermally exposed to paint while changing the paint booth filters and adjusting the spray guns. Paint residue was observed on all mixing equipment in both paint mix areas (near cascade line 2 and near DD lines 1 and 2) and on all interior surfaces of the paint booth. Only one worker was observed wearing gloves (nitrile) while mixing the paint. While they were changing the paint booth filters, workers were observed wearing cotton gloves and, in some cases, a half-face, air-purifying respirator with dual organic vapor and dust/mist cartridges. Workers did not wear any personal protective equipment while adjusting the spray guns in the paint booths except for the occasional use of latex gloves. In general, paint was mixed once per day per line and the paint booth filters were changed once per day. The spray guns were adjusted throughout the work shift, depending on air temperature and humidity.

Medical

The 15 participants in the evaluation of contact dermatitis consisted of 13 men and 2 women. Eight worked the first shift and seven the second. The average age of the participants was 35; participants averaged six years working at their current job. The job titles of participants included operator (3), utility incentive (10), and maintenance mechanic (1). One of the participants (who was a utility incentive at the time symptoms began) had been moved out of the DD area due to persistent skin rashes and occupational asthma. None had a significant dermatitis present at the time skin patch testing was performed.

Three workers had skin test reactions suggestive of allergy. One had a 3+ reaction to mercaptobenzothiazole, one had a 2+ reaction to carba mix, and one had a 2+ reaction to neomycin. Mercaptobenzothiazole and carba mix are substances most commonly used as rubber additives (accelerators). Review of the rubber formulations used in the DD department revealed that both substances were present in several rubber formulations used to make the vehicle sealing. Subsequent interviews revealed that the worker with the reaction to mercaptobenzothiazole had a history of skin reactions to rubber boots. Neomycin sulfate is a commonly used antibiotic and has no known connection to potential occupational exposures at Cooper.

One worker had an irritant reaction to the aziridine and to the polyurethane component of the paint, but not to the aziridine–polyurethane mixture. The irritation was manifested as redness at the corresponding skin patch sites at the time of the 48-hour interpretation, which had completely resolved by the time of the 96-hour interpretation. Because only one participant demonstrated an irritant response to the paint components (which are known irritants at full strength), the mixtures were adequately diluted (0.1%) to prevent irritant reactions in most individuals. It is likely that the above participant has skin highly sensitive (though not allergic) to those substances.

There was no residual redness (at 48 or 96 hours) on the skin of any of the participants who had been affected by the irritant–type reaction to benzoin.

CONCLUSION

N–methyl pyrrolidone was used as an indicator of relative levels of exposure to the water–based polyurethane paint because it was a major compound identified in of the bulk paint samples and the TD tube air samples. Utility incentives who worked with the paint and in the paint booths had mean inhalation exposures to NMP (0.15 ppm) almost 4 times those who did not (0.04 ppm). NMP exposures of operators were similar to utility incentives who did not work with the paint or paint booths. Workers in the DD department may also be exposed to low levels (below 1 ppm) of propylene glycol, carbon disulfide, and xylenes. Air concentrations of isocyanates and nitrosamines were below their MDCs of 1.6 $\mu\text{g}/\text{m}^3$ and 0.028 $\mu\text{g}/\text{m}^3$, respectively. The health hazards associated with the measured levels of NMP are not clear because only limited occupational exposure data are available, and exposure limits have not been established.

Utility incentives were dermally exposed to irritants and a sensitizer in the paint, especially when they changed the paint booth filters and adjusted the spray guns. One worker was observed wearing cotton gloves while performing these activities, but cotton gloves will not adequately protect workers' hands from exposure to the paint.

Two DD workers, each of whom had a history of work–related skin rashes, had skin patch test reactions suggestive of allergy to accelerators present in the rubber used at Cooper. Although it is likely that these allergies are playing a significant role in these two workers' skin problems, there may be an irritant component to their skin problems as well.

Only 15 workers participated in the patch testing, and there are at least 15 other DD workers with possible work–related skin problems about whom we

can draw no diagnostic conclusions. Because no participants were found to be allergic to aziridine, it is likely that most participants' work-related skin problems are related primarily to exposure to one or more irritants present in the department (causing irritant contact dermatitis). The irritant substance(s) to which most DD workers are most likely to have repeated skin exposure are constituents of the paint used on the rubber seals. Alternatively, and less likely based on our review of the process, there could possibly be other substances not included in the patch testing in the DD area that are causing allergic contact dermatitis among the participants.

The reactions NIOSH medical officers observed related to the application of benzoin to the skin, though reported previously, are unusual.^{26,33,34} There is no evidence that these reactions have any bearing on skin problems reported in the DD area.

RECOMMENDATIONS

Based on the results and observations of this investigation, the following recommendations are offered to reduce the occurrence of dermatitis caused by exposures to the vehicle sealing and the water-based polyurethane paint.

1. Workers who have allergies to rubber additives should minimize exposure to rubber containing those additives. If avoiding all contact with rubber is not possible, the use of cotton (when handling rubber) or other non-rubber impervious gloves (when potentially exposed to liquids such as the paint) may be adequate to prevent dermatitis due to those allergies.

2. In general, a combination of the following strategies should be used to prevent occupational skin diseases in the DD area:

- a) Identify irritants and allergens in the workplace.

- b) When feasible, and considering systemic as well as dermatologic toxicity, substitute chemicals that are less irritating/allergenic.
- c) Establish engineering controls and increase housekeeping to reduce skin exposure. In particular, efforts should be made to decrease skin exposure to the paint when changing filters and adjusting spray guns in the paint booths, and during mixing operations. In the paint booths, roll filters could be installed so workers do not have to enter paint booths to change filters. In the print mix areas and paint booths, all equipment used to mix or spray paint should be cleaned periodically to prevent paint buildup.
- d) Utilize personal protective equipment such as gloves and special clothing to reduce skin exposure to the paint and rubber products (item 3 below).
- e) Emphasize personal and occupational hygiene (items 4 and 5 below).
- f) Establish educational programs to increase worker awareness of irritants and allergens in the workplace.
- g) Provide a system for the evaluation, reporting, and surveillance of dermatologic diseases (item 6 below).

3. Skin should be protected from contact with irritants and allergens (sensitizers) with proper personal protective equipment such as clean gloves, protective coveralls, and sleeve protectors. Glove selection should be based on information in the specific material safety data sheets and other guidelines. For NMP, butyl rubber gloves are preferred.³⁵ Appendix 2 provides information from one reference regarding allergens present in specific gloves.³⁶ Particular attention should be given to the carbamate and benzothiazole columns. Gloves that have these compounds should not be used by workers who had allergic reactions to mercaptobenzothiazole and the carba mix.

4. Irritants and allergens that have come in contact with exposed skin should be washed off with soap and water as soon as possible. Residual soap should be washed off the skin surface. Special attention should be directed toward soaps and skin cleansers since they themselves can serve as irritants. Certain components of the soaps or moisturizers (e.g., lanolin and fragrances) are known allergens and may cause allergic contact dermatitis in sensitive individuals.

5. Before a worker leaves the work site, clothing potentially contaminated with irritants or allergens should be removed. It should be laundered prior to re-use (preferably by Cooper). Contaminated clothes should be laundered separate from street clothes.

6. Workers should be encouraged to continue to report all possible work-related skin problems. These problems should be investigated on an individual basis by the company and consulting health care providers. Because the work-relatedness of skin diseases may be difficult to prove, each person with a possible work-related skin problem needs to be fully evaluated by a physician, preferably one with expertise in occupational/dermatological conditions. A complete evaluation would include a full medical and occupational history, a medical exam, a review of exposures, possibly diagnostic tests (such as skin patch tests to detect causes of allergic contact dermatitis), and complete follow-up to note the progress of the individual. Individuals with definite or possible occupational skin diseases should be protected from exposures to presumed causes or exacerbators of the disease. In some cases, reassignment to areas where exposure is minimized or nonexistent may be medically advisable. In such cases, the reassigned worker should retain wages, seniority, and other benefits that might otherwise be lost by such a job transfer.

7. Although a respiratory protection program was in place at Cooper, one worker who had a significant amount of facial hair was wearing a respirator. Workers should be restricted from having any facial hair that comes between the sealing surface of the facepiece and the face. The respiratory protection

program must, at a minimum, comply with the requirements described in the OSHA respiratory protection standard (29 CFR 1910.134).³⁷ Publications developed by NIOSH can also be referenced when developing an effective respirator program, including the NIOSH Guide to Industrial Respiratory Protection and the NIOSH Respirator Decision Logic.^{38,39}

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TABLE 1

N-methyl Pyrrolidone PBZ and Area Air Sample Results
Cooper Engineered Products
HETA 96-0266-2702

* All sample concentrations are presented in parts per million (ppm).

Job Task	Number of Samples	Mean*	Range*
PBZ air samples			
Utility incentives – adjust spray guns, change paint booth filters, and mix paint.	26	0.15	0.01 – 1.27
Utility incentives – did not work with paint or paint booth	19	0.04	0.01 – 0.15
Operators	3	0.02	0.01 – 0.03
Area air samples			
Paint booths:	Inside	6	12.0
	Outside	8	0.05
Cascade paint mix area	3	0.10	0.04 – 0.20
Lunch area	3	0.02	0.01 – 0.03

APPENDIX 1

Substances included as potential allergens in skin patch testing at Cooper Engineered Products.

Standard Patch Test Kit

Benzocaine, 5% in petrolatum
Mercaptobenzothiazole, 1% in petrolatum
Colophony, 20% in petrolatum
p-Phenylenediamine, 1% in petrolatum
Imidazolidinyl urea, 2% in water
Cinnamic aldehyde, 1% in petrolatum
Lanolin alcohol, 30% in petrolatum
Carba mix, 3% in petrolatum
Neomycin sulfate, 20% in petrolatum
Thiuram mix, 1% in petrolatum
Formaldehyde, 1% in water
Ethylenediamine dihydrochloride, 1% in petrolatum
Epoxy resin, 1% in petrolatum
Quaternium 15, 2% in petrolatum
p-tert-Butylphenol-formaldehyde resin, 1% in petrolatum
Mercapto mix, 1% in petrolatum
N-Isopropyl-N'-phenyl paraphenylenediamine, 0.1% in petrolatum
Potassium dichromate, 0.25% in petrolatum
Balsam of Peru, 25% in petrolatum
Nickel Sulfate, 2.5% in petrolatum

Specially-prepared Substances for Patch Testing

cx100 (aziridine), 0.1% in water
polyurethane component of paint, 0.1% in water
cx100/polyurethane paint mixture (1:36), 0.1% in water
cx100 (aziridine), 0.1% in petrolatum

APPENDIX 2



Delivering on the Nation's promise:
• **Safety and health at work for all people
through research and prevention**